Chapter XI

Cellular Automaton Models of Reaction-Transport Processes

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XI.1. Introduction

In many processes occurring in geological media mass transport and chemical reactions are intricately connected. The range of these processes includes natural phenomena, such as the chemical weathering of rocks and the diagenetic changes caused by ground-water flow, as well as procedures of technological interest, such as oil recovery and containment of contaminant migration. In case of a failure in a nuclear waste repository, the released radionuclides will be transported by flowing water, while they decay radioactively, sorb on solid surfaces and react chemically with each other and the host rock. Modelling coupled transport and chemical reactions in their full complexity is a formidable task and a great deal of ingenuity is required to identify the most important features and processes in any given situation.

In spatially extended geological systems, however, complexity at the macroscopic level need not reflect particularly intricate aspects of the microscopic dynamics. On the contrary, it is well-known that relatively simple microscopic properties can lead to very rich macroscopic behaviour. Thus, the motion of fluids (laminar and turbulent flow, shock waves, flow in porous media) can be understood in terms of local mass, momentum and energy conservation. The random collisions of the molecules of a few chemical species in solution can couple with their chemical reaction kinetics to produce a wide variety of

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striking behaviour (oscillations of the concentrations in time, stationary spatial patterns or non-linear travelling waves).

In theoretical models of such phenomena the essential microscopic properties are usually embedded in macroscopic partial differential equations (e.g., the continuity equation and the Navier-Stokes equations for fluid motion or the reaction-diffusion equations for the concentrations of dissolved species). The macroscopic attributes described by these equations (fluid velocity, solute concentration) are related to the underlying microscopic quantities by an averaging operation which extends over a volume element small on the typical volume scale of interest, but large compared with the average volume per molecule. In the process of averaging, such information as microscopic fluctuations is discarded. A basic premise of the macroscopic approach is that spatial and temporal variations are sufficiently slow for different parts of the system to be assumed in a state of local thermodynamic equilibrium at all times. The macroscopic equations are usually non-linear and have to be solved numerically. When iterating a numerical algorithm in a computer, round-off errors (arising when real numbers are truncated to finite computer words) can accumulate exponentially, leading to overflows. Guaranteeing the stability of numerical algorithms is a tedious procedure for non-linear problems. In contrast to the macroscopic approach, molecular dynamics deals with the motion of individual molecules under the influence of realistic intermolecular potentials. In this approach one addresses problems of a more fundamental nature, such as understanding at a molecular level the phenomenological coefficients of macroscopic models [80BOO/YIP]. Obviously the length and time scales relevant to molecular dynamics are much shorter than those typical of a macroscopic description.

There is a large class of problems involving natural systems that lie in the intermediate region between the macroscopic and the microscopic description. These naturally include problems with a characteristic length scale that is much larger than that of molecular events ($\sim 1 \, \text{Å} = 10^{-8} \, \text{cm}$), but also much smaller than macroscopic length scales (for example, bulk properties of a rock, such as porosity, can be typically defined on a scale of $\sim 1 \, \text{cm}$). We refer to such an intermediate scale as mesoscopic. Thus, processes taking place at pore level in a rock (typical pores have linear dimensions of the order of $100 \, \mu \text{m} = 10^{-2} \, \text{cm}$), such as changes in porosity due to precipitation/dissolution, belong intrinsically to this intermediate class of problems. Differential equations have been employed in mesoscopic modelling of natural systems, but only under convenient assumptions concerning the often very irregular boundaries (by assigning, for example, the flow in porous media to a network of capillary tubes of simple geometry [92DUL]). Even at typically macroscopic scales some kind of intermediate description may be indispensable when the complexity of the boundary conditions or the variability of certain quantities in space and time call for a degree of detail that cannot be afforded by the standard macroscopic equations.

The type of problems addressed at field scale (several metres or more) are of a very different nature from those solved by typical mesoscopic models. The spatial discretisation appropriate for field-scale problems is much coarser than the spatial detail that has to be accounted for at the mesoscopic scale. This is dictated in the first place by reasons
of computational feasibility, but also and most importantly for conceptual reasons: the evolution equations for macroscopic quantities, such as solute concentrations, can usually be expressed in terms of macroscopic bulk parameters, which are defined by averaging out finer details. Contact between modelling at different scales is established at the interface where mesoscopic models provide the relations between bulk parameters and their evolution in time, which cannot be derived or are known only empirically at the macroscopic level. The same is true about different time scales, where the times typical of geological phenomena may often render irrelevant the kinetics of specific reactions. As we shall see later in this chapter, there are notable exceptions where certain phenomena cannot be modelled in terms of purely macroscopic parameters and a mesoscopic description is indispensable, irrespective of the computational resources that this may require.

In this chapter we are going to present a new and promising method of modelling mass transport and chemical reactions at the mesoscopic level. The basic concept in this approach is that of a cellular automaton, i.e., a dynamical system consisting of an integer field defined on the sites of a regular spatial lattice and evolving in discrete time steps according to a local updating rule; the rule determines the new value of the field at a certain site of the lattice according to the current values of the sites within a neighbourhood surrounding the site in question [86WOL]. In the case of a system of dissolved species migrating in a porous or fractured medium and reacting with each other as well as with the host rock, one can think of the lattice as spanning the rock volume of interest and the local rule as modelling the collisions and the chemical reactions of the solute particles. Transport and chemical reactions are modelled in a way that preserves a limited number of microscopic features (most notably, microscopic fluctuations and correlations, as well as reaction kinetics), which are expected to influence the macroscopic behaviour we wish to describe. Moreover, since the behaviour of the solute particles upon contact with the solid boundaries is modelled in a physically motivated manner, the complexity of the boundaries has no bearing on modelling feasibility or even computational efficiency. The synchronous evolution of a cellular automaton reflects the local and parallel character of the natural processes it models: molecules migrate and react simultaneously at different locations inside the rock and each molecule reacts only with molecules in its immediate neighbourhood. The parallel and local properties of cellular automata map naturally onto the architecture of massively parallel computers. In the latter, a large number of processors (up to several tens of thousands) run in parallel, manipulating data from their local memories; data are transferred between processors via sophisticated communications networks which are particularly efficient for transfers between neighbouring processors. Massively parallel architectures are expected to dominate the design of new computers in the coming years since they offer the only way to improve by orders of magnitude, on the performance of current scalar and vector computers (it takes an electromagnetic signal some nanoseconds to traverse a typical length of 1 m and this sets an absolute upper limit to the clock frequency of serial processors).

The remainder of this chapter is organised as follows: The development of cellular automata (CA) from their initial inception as models of biological systems, to their present implementation in the simulation of a wide range of physical phenomena is outlined in
the next section. In the same section we illustrate the basic concepts with the help of elementary examples. Following that, we present CA models for coupled transport and chemical reactions and describe their applications to reaction-transport systems ranging from the simplest and better understood to increasingly more complex and realistic ones. In the final section we evaluate the potential of the CA approach and indicate possible future developments. It should be emphasised that this chapter has a rather pedagogical orientation. The author will allow a certain personal bias in the selection and presentation of the relevant material and does not expect this work to be seen as a review article, even more so since reviews and extensive compilations of articles are already available [84FAR/TOF, 89MAN/BOC, 90GUT, 95CHE/DAW].

XI.2. Cellular automata

XI.2.1. Historical development

The theory of automata was envisaged by John von Neumann as a systematic mathematical and logical framework that would unify the basic principles of natural and artificial information processing systems [87ASP/BUR, 90ASP]. The idea of a unified approach appeared in the early days of the digital computer and was motivated by the plausible analogy between computers (as well as other communications and control devices) and self-regulating biological systems (cells, the human nervous system, organisms capable of reproduction and evolution). Typical questions addressed were those of reliability (i.e., the ability to detect errors and minimise their effect) and of the minimal complexity that enables an automaton to construct other, equally complicated automata. A universal constructor, i.e., an automaton that can construct any other automaton would be equivalent to the universal Turing machine, the theoretical prototype of a general-purpose computer. A computer A is called “universal” if, given any other computer B, there is always an appropriate piece of software which enables A to emulate B in the sense that the two devices deliver the same output for any given input [89PEN]. Following initial difficulties with a three-dimensional kinematic automaton that would physically assemble its duplicate out of a pool of elementary parts, von Neumann heeded the advice of Stanislaw Ulam and considered the abstract setting of cellular automata, i.e., two-dimensional square arrays of cells, each of which assumed one out of the same finite set of states. Although cellular automata could be directly translated into parallel computer structures in theory, the size and power consumption of hardware components available at the time rendered a physical implementation of the cellular automaton paradigm impractical. Interestingly, von Neumann’s name is usually associated only with the serial computers developed in his lifetime; essentially, he also laid the theoretical foundations for the massively parallel computers built later, when integrated circuit technology drastically enhanced the processing and memory storage capacity of single chips.

Although von Neumann’s program of a comprehensive theory of automata was never

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2 It is possible that other people arrived at similar ideas independently (see, e.g., [69ZUS]), but von Neumann’s work is by far the most extensive, albeit itself incomplete, on published record.
Cellular automata (CA) developed their own dynamic in the 1970's and 1980's. Information concerning CA implementations in special-purpose hardware and general-purpose computers can be found in Refs. [84HILL, 84PRE/DUF, 87TOF/MAR, 90BOG]. Largely as a result of the ongoing dramatic rise in available computing power in general, and the advent of massively parallel computers in particular, CA algorithms are increasingly employed to simulate natural phenomena. A wide field of applications opened when CA were applied to the simulation of fluid dynamics [90DOO/FRI, 91DOO], following the realisation that a certain class of CA approximate the Navier-Stokes equations [86FRI/HAS]. The CA of this class have come to be known as lattice gas automata (LGA). A wide range of flow phenomena have been modelled in the meantime, including the flow of multiphase mixtures (e.g., oil and water) [88ROT/KEL, 91SOM/REM] and phase transitions (e.g., liquid-gas) [90APP/ZAL, 93APP/ZAL], turbulence [88SUC/SAN], magnetohydrodynamics (i.e., the motion of electrically conducting fluids, such as plasmas, in the presence of a magnetic field) [87CHE/MAT, 87MON/DOO], colloidal suspensions [88LAD/COL] and flow in porous media [87BAL/HAY, 88ROT]. Due to the simplicity of their dynamics, LGA have been used as models to address fundamental problems in kinetic theory, such as the long-time behaviour of time correlation functions [76HAR/PAZ, 89FRE, 89FRE/ERN] and the relation of transport coefficients (e.g., viscosity, thermal conductivity) to the time integral of correlation functions [87RIV, 90ERN/DFU, 92ERN/DAS]. CA have also been used to model various physicochemical processes of engineering interest (carbonation of concrete [91BRI/BON], catalytic CO(g) oxidation on platinum surfaces [92WU/KAP], polymer chains in solution [90VIA/KOE], charged-particle transport in semiconductors [92KOM/ZAN]), biological functions (e.g., the immune response [85KAU/URB] or the biochemistry of the cell [93HAS/KAP]) and astrophysical phenomena [93PER/LEJ].

What interests us here are CA simulations of systems of molecules that move by means of diffusion and/or advection and react chemically with each other and with the surrounding medium (e.g., reactive chemicals diffusing in a gel or solutes migrating in a porous medium). CA models of mass transport with chemical reactions were developed either along lines similar to the LGA models of fluid dynamics [89DAB/BOO, 90DAB/LAW, 91LAW/DAB] or independently [90BLA, 93KAR, 94KAR/BLA]. Before we describe these models in detail, we shall illustrate the basic concepts by means of a few elementary examples, which will also demonstrate the capacity of simple CA rules to produce interesting complex behaviour.

XI.2.2. Elementary examples

“Life” is a mathematical game, in which a two-dimensional square array of cells displays a lot of the lively activity typical of an assembly of living organisms [70GAR]. Beginning with some initial configuration of live cells (state ‘1’), one follows the evolution of the

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6 Although there is no general prescription for finding the microscopic rules that will simulate a given set of macroscopic equations, the CA approach has been applied to the numerical solution of various partial differential equations of physical interest [87BOG/LEV, 88CHE/CHE, 90CHE/MAT].
population as previously dead sites (state ‘0’) come to life (if there are exactly 3 live cells among the 8 neighbours on the square surrounding them) and live cells persist (if 2 or 3 of their 8 neighbours are alive) or die (otherwise). This evolution rule was chosen by John Conway, the inventor of the game, so as to avoid the more common scenarios of rapid uncontrolled growth or extinction of the population. Typical snapshots from the evolution of an originally random population of 50% live cells are shown in Fig. XI.1. Following an initial burst of activity and occasional later flares, most configurations settle down to a sparse distribution of stationary and oscillating patterns (last frame in Fig. XI.1). Propagating patterns (“gliders”) and configurations that grow without limit (“glider guns”) are less common, but contribute to the unpredictability of “Life”. When a glider meets another group of live cells a new pattern is in general created. Thus glider crashes can be designed to produce glider guns, which in turn emit streams of fresh gliders. An “eater” is a pattern that annihilates other patterns upon colliding with them. One can build logical gates (NOT, AND, OR) out of glider guns and eaters. It turns out that one can construct an arbitrary computer out of such gates, so that “Life” is capable of universal computation in the sense of the universal computer defined in Section XI.2.1 [82BER/CON]. It is a remarkable fact that a CA with no more than two possible states per site and a very simple evolution rule can perform all the complicated tasks that a general-purpose computer can.

As a second example we mention the CA implementation of the “billiard-ball” model of computation. In the latter, the elastic collisions of a gas of hard spheres with each other, and their reflections by a set of “mirrors” are used to construct a universal computer [82FRE/TOF]. We consider a square lattice of cells, as before, each with two possible states and we divide them in $2 \times 2$ blocks. Given such a partition of the lattice, we define the updating rule of a $2 \times 2$ block as specified in Fig. XI.2a (complemented with all possible rotations of the transitions indicated) [84MAR2]. Between successive applications of the rule, we shift the partitioning grid along the diagonal by $\sqrt{2}$ times the lattice spacing (from the solid to the dashed lines in Fig. XI.2b, where the legend “solid” or “dotted” indicates the partitioning for the next application of the rule). If we let ‘1’s and ‘0’s denote particles and empty sites respectively, iteration of the above rule makes particles propagate and collide elastically with each other (Fig. XI.2b). Two adjacent blocks filled with particles form a stable configuration that acts as a mirror. It has been shown [84MAR2] that the CA we have just described is equivalent to the billiard-ball model and is consequently a universal computer. This is an example of a reversible CA, i.e., one whose evolution can be traced backwards in time, in direct analogy with the microscopic reversibility of physical laws. The realisation that reversible universal computers are feasible has far-reaching implications for the physical limitations of computers, since it appears to remove the lower boundary on dissipation associated with standard irreversible logic elements [73BEN, 84MAR2].

As a last example, we show in Fig. XI.3 different stages in the evolution of a CA which develops spatial structures similar to the concentration patterns observed in certain chemical experiments. The simulation is performed with a triangular lattice of cells that exist in three different states: “activated” (white), “receptive” (black) and “quiescent” (grey).
Cellular automata

During one update, all receptive cells among the nearest neighbours of an activated cell become active, while the activated cell itself turns quiescent. A quiescent cell cannot be excited until it becomes receptive after two time steps [83MAD/FRE]. Different patterns, such as circular waves and spirals, develop depending on the initial configuration. The one- and two-armed spirals in Fig. XI.3 arise from isolated lines of active cells buffered by lines of quiescent cells. It can be seen that, when the spirals collide, they halt each other along their line of contact, but continue to spread unhindered elsewhere. Similar patterns have been observed in experiments with autocatalytic chemical reactions [72WIN, 73ZHA/ZAI]. We are going to return to the subject of autocatalytic reactions in the next section.

Having seen how simple CA can simulate the motion and collisions of particles, as well as effects reminiscent of complex chemical systems, we can now proceed to describe in
Figure XI.2: (a) Updating rule for CA implementation of “billiard-ball” model of computation; (b) Propagation and collision of particles according to this rule (reprinted with permission from Ref. [84MAR2], Figs. 4 and 12).
Cellular automata for transport with chemical reactions

Figure XI.3: One- and two-armed spirals evolving out of isolated lines of activated cells (white) buffered by lines of quiescent cells (grey).

more elaborate CA models that couple these processes.

XI.3. Cellular automata for transport with chemical reactions

XI.3.1. Models

XI.3.1.1. Transport

From a macroscopic point of view, solutes migrate in a porous medium by means of advection, molecular diffusion and kinematic dispersion [86MAR3]. Advection takes place when a solute is carried along by the flow of the solvent; it is characterised by a velocity, which, for sufficient dilution, coincides with the Darcy velocity of the pure solvent. Molecular diffusion is the macroscopic manifestation of the Brownian motion of the solute particles caused by random impacts with fluid molecules; in an ideal solution it is described by Fick’s law, which introduces the coefficient of molecular diffusion. Finally, kinematic dispersion is the spreading of the solutes around the mean advective displacement due to microscopic variations in flow velocity inside individual pores, but also between pores of different aperture and length; kinematic dispersion is commonly accounted for in the transport equation by a diffusion term, which can be combined with the analogous term for molecular diffusion to define an effective overall diffusion coefficient. In what follows, we shall use “diffusion” to describe the combined effect.

The breakdown of transport into advection and diffusion is rather arbitrary and becomes
Cellular Automaton Models of Reaction-Transport Processes

less meaningful as we focus on the finer structure of the porous medium. At the mesoscopic level, particle transport can be thought of as a single process which consists of a collection of particles performing independent random walks. We assume that particles move between the sites of a regular spatial lattice. In discrete time steps, particles jump to one of their nearest-neighbour sites with a certain probability. If the particles jump in all directions with the same probability, then the random walk manifests itself at the macroscopic level as pure diffusion. If on the other hand particles tend to jump preferentially in a given direction, this leads macroscopically to combined advection (in the favoured direction) and diffusion. We consider for simplicity a one-dimensional lattice, since extensions to higher dimensions are straightforward. Let the lattice spacing and the time step be \( \lambda \) and \( \tau \) respectively. We refer to sites on the lattice by their location in space, e.g., site \( x \). During one time step, each particle moves to the next site on the right with a certain probability \( p \), to the next site on the left with probability \( q \) (of course \( p + q \leq 1 \)) or remains stationary, with probability \( 1 - p - q \). It is useful to see the system as a fixed array of sites; the state of site \( x \) at time \( t \) is given by the integer field \( N(x, t) \), the number of particles at that site, at the given time; the evolution of \( N(x, t) \) is determined by the rule defining the random walk. The array of sites, together with the integer field and the evolution rule, constitute a CA that models the transport of solute particles.

We run the simulation on an ensemble of lattices subject to the same mesoscopic laws (i.e., same \( p \) and \( q \)), with macroscopically identical initial and boundary conditions. Let us first assume that \( p \) and \( q \) are constant in space and time. If we define the particle density \( \rho(x, t) \) as the ensemble average of \( N(x, t) \), it can be easily seen that \( \rho \) evolves in time according to the difference equation

\[
\rho(x, t + \tau) = p\rho(x - \lambda, t) + (1 - p - q)\rho(x, t) + q\rho(x + \lambda, t)
\]

which can be readily rearranged to

\[
\frac{\rho(x, t + \tau) - \rho(x, t)}{\tau} = -V \frac{\rho(x + \lambda, t) - \rho(x - \lambda, t)}{2\lambda} + D \frac{\rho(x + \lambda, t) - 2\rho(x, t) + \rho(x - \lambda, t)}{\lambda^2},
\]

with the parameters \( V \) and \( D \) defined as

\[
V \equiv (p - q) \frac{\lambda}{\tau}, \quad D \equiv (p + q) \frac{\lambda^2}{2\tau}.
\]

\[4\] We intentionally talk about solute “particles” and their “density”, rather than about solute “molecules” and “concentration”, as it is clear that, in the foreseeable future, the number of particles in all CA simulations of experimentally or naturally realisable processes must, for practical reasons, fall short of the number of molecules actually involved by several orders of magnitude. Contact with the real process is established by rescaling the density at the level of the output [93KAR, 94KAR/BLA].
If we take the continuum limit $\lambda \to 0$, $\tau \to 0$ and $p - q \to 0$, while keeping $\lambda^2/\tau$ and $(p - q)\lambda/\tau$ finite, Eq. (XI.2) goes over to the transport equation

$$\frac{\partial \rho(x, t)}{\partial t} = -V \frac{\partial \rho(x, t)}{\partial x} + D \frac{\partial^2 \rho(x, t)}{\partial x^2} . \tag{XI.4}$$

The right hand side of Eq. (XI.4) contains an advective and a diffusive term. We identify $V$ as the *advection velocity* and $D$ as the *diffusion coefficient*. The continuum limit is taken in such a way that $V$ and $D$, as defined by Eq. (XI.3), remain finite. Eq. (XI.2) is the forward-time centred-space finite difference approximation to the transport equation (XI.4). It is clear that, by making $p$ and $q$ species dependent, we can have species with different transport properties move on the same lattice. If $V$ and $D$ are not homogeneous, the system can be modelled by making $p$ and $q$ position dependent (then, if $V$ and $D$ are defined according to Eq. (XI.3), the advection velocity has to be defined by $\tilde{V}(x) \equiv V(x) - dD(x)/dx$).

Boundary conditions are modelled by mimicking the behaviour of actual molecules when they reach boundaries with the specified properties. Thus, when particles reach an impermeable boundary, they bounce back or remain stationary. The “free-flow” boundary condition, according to which only advection carries particles across the boundary ($\partial \rho(x, t)/\partial t = 0$, for $x$ at the boundary), is simulated by cancelling the outgoing diffusive flux with an equal and opposite diffusive flux, coming from a fictitious reservoir on the other side of the boundary. A fixed density at the boundary is modelled by choosing the number of particles at boundary sites from a distribution consistent with the specified average value; this simulates the situation where the boundary sites are in contact with a particle reservoir of the appropriate density. A periodic boundary condition is often computationally convenient and is justified when the precise behaviour of the boundary sites is not important, *e.g.*, with translationally invariant homogeneous systems or when the boundary is too far away to influence the region of interest.

In a typical simulation of the kind described above, it cannot be excluded that, at a certain point in the simulation, a large number of particles are found at the same lattice site. Given the total number of particles initially present and the rate at which particles enter and leave the system, an upper limit can be calculated in advance of the simulation. This limit is however of little value in practice since it is highly unlikely to ever be reached in an actual simulation. It is often desirable in computer simulations to allow *a priori*, only a limited number of particles per site. This makes it possible to program at bit level and construct look-up tables of all conceivable input-output combinations that may occur at a site. One is then able to produce very efficient CA simulations on dedicated hardware [87TOF/MAR], but also to substantially improve performance on serial and vector computers [90SHI/DOO]. A restriction to the the number of particles per site is imposed in LGA models of fluid dynamics in the form of an *exclusion principle*: a small number of velocities are assigned to each lattice site (*e.g.*, in a single-speed model, the vectors of magnitude $\lambda/\tau$ pointing to the nearest neighbours) and at most one particle per site is allowed to have a given velocity. As a result, the state of an LGA is defined by
a Boolean field that gives the occupation numbers (0 or 1) of the velocity states at each site.

One can also model diffusion with very efficient CA algorithms which obey an exclusion principle [91CHO/DRO]. We consider again a one-dimensional lattice and assign two possible velocities to each site: \( \mathbf{c}_1 = (\lambda/\tau)\hat{e}_1 \) pointing to the right and \( \mathbf{c}_2 = (\lambda/\tau)\hat{e}_2 \) to the left (\( \hat{e}_1 \) and \( \hat{e}_2 \) are unit vectors). One evolution step of the automaton consists of two elementary operations: First, a rotation operator acts independently on different nodes and causes the velocity configuration at each of them to remain intact or rotate by \( \pi \) with probability \( p \) and \( 1 - p \), respectively; following this, particles propagate to the next lattice site along the direction of their velocity. Let the Boolean variable \( N_i(x,t) \) denote the number of particles with velocity \( \mathbf{c}_i \) at site \( x \) and time \( t \). Then the ensemble average \( \rho_i(x,t) \) of \( N_i(x,t) \) satisfies the discrete evolution equation

\[
\begin{pmatrix}
\rho_1(x,t + \tau) \\
\rho_2(x,t + \tau)
\end{pmatrix} = p \begin{pmatrix}
\rho_1(x - \lambda, t) \\
\rho_2(x + \lambda, t)
\end{pmatrix} + (1 - p) \begin{pmatrix}
\rho_2(x - \lambda, t) \\
\rho_1(x + \lambda, t)
\end{pmatrix}.
\]

(Eq. (XI.5))

The first (second) term on the right hand side of Eq. (XI.5) accounts for particles that propagate to the next site without (after) being rotated. We define the particle density \( \rho(x,t) \equiv \sum_i \rho_i(x,t) \).

Since the number of particles is conserved, a continuity equation holds in the form

\[
\rho(x,t) - \rho(x,t - \tau) + \sum_{i=1}^2 J_i(x,t) = 0,
\]

(Eq. (XI.6))

where \( J_i(x,t) \equiv \rho_i(x + \lambda\hat{e}_1,t) - \rho_{3-i}(x,t) \) is the net flux of particles traversing the lattice link from \( x \) to \( x + \lambda\hat{e}_1 \) in the time between \( t - \tau \) and \( t \). Taking the continuum limit of Eqs. (XI.5) and (XI.6) (\( \lambda \rightarrow 0, \tau \rightarrow 0 \), keeping \( \lambda^2/\tau \) finite), we arrive, after some simple algebraic manipulations, at the diffusion equation (Eq. (XI.4) without the advection term) with

\[
D \equiv \frac{p}{1 - p} \cdot \frac{\lambda^2}{2\tau}.
\]

Species with different diffusion coefficients can be simulated on the same lattice by adjusting \( p \). Diffusion in two and three dimensions is treated in Ref. [91CHO/DRO]. The advantage of this algorithm is that it can be readily implemented on special-purpose computers and its performance on vector supercomputers exceeds that of the previous algorithm by more than an order of magnitude. On the other hand, the exclusion principle induces correlations between particles and these in turn give rise to non-linear terms in the transport equations derived from models with biased random walks [87BOG/LEV]. As a result, models with an exclusion principle are not able to model advection without introducing at the same time unwanted terms in the transport equation.

Modelling diffusion and advection with CA would be an exercise of little practical interest, were it not to be coupled with chemical reactions, a task that we immediately proceed to fulfil.
XI.3.1.2. Chemical reactions

In the full coupled problem, an evolution step consists of a transport operation followed by a chemical reaction operation. We first consider a system with no restriction on the number of particles per site. Transport takes place as described above for such a system. Particles of various solute species move on the lattice and, when sufficient numbers of them meet at a site, they react with a certain probability. A reaction is more likely to occur the more the particles of each reactant that are present. If a reaction takes place, then the appropriate number of products (reactants) are added to (subtracted from) the local inventory of particles.

We consider a system of species \( s_a \) and reactions \( r \). We write all reactions in the one-way form by separating, in the case of reversible reactions, the forward from the reverse process:

\[
\sum_a \nu_{or,i} s_a \rightarrow \sum_a \nu_{or,f} s_a
\]  

(XI.8)

where \( \nu_{or,i} \) and \( \nu_{or,f} \) are the stoichiometric coefficients of the initial and final state of the reaction, respectively. The summations run over all species, but the \( \nu_{or,i} \) (\( \nu_{or,f} \)) vanish for species not present among the reactants (products). If reaction \( r \) involves only species in solution, we let it proceed with probability

\[
P_r \prod_{a=1}^{\nu_{or,i}} (N_a(x,t) - m + 1) ,
\]  

(XI.9)

where \( P_r \) is a constant and \( N_a(x,t) \) is the number of particles of species \( s_a \) at site \( x \) and time \( t \). For example, if \( r \) is the reaction \( a + 2b \rightarrow c \), it takes place with probability \( P_r N_a N_b (N_b - 1) \). Of course, the reaction probability has to be \( \leq 1 \); since \( N_a \) and \( N_b \) are finite in a simulation, we can always ensure that \( P_r N_a N_b (N_b - 1) \leq 1 \) by choosing \( P_r \) sufficiently small. We shall see shortly that it is the ratio \( P_r/\tau \) that is physically meaningful, so \( \tau \) has to be chosen correspondingly small, with a concomitant increase in the number of iterations. In the case of reactions between solutes and mineral surfaces, the reaction rule has to be modified so that precipitation takes place with a probability defined as before, but only if solid is already present or the solution is saturated.

We wish to derive an evolution equation for the particle density \( \rho_a(x,t) \), defined as an ensemble average of \( N_a(x,t) \). To this end we have to make two important assumptions. In evaluating the average of the product in Eq. (XI.9), we assume that there are no correlations between the \( N_a \) for different species (molecular chaos). The resulting simple averages (e.g., \( \overline{N_b(N_b - 1)} \) in the example above) can be expressed in terms of the densities, if the \( N_a \) do not vary appreciably over several lattice spacings (smoothness assumption); then we can evaluate \( \rho_a(x,t) \) by averaging locally around \( x \) over a uniform distribution of particles (the crucial fact is that, for a uniform particle distribution, \( N_a(x,t) \) obeys a Poisson distribution parametrised with \( \rho_a(x,t) \) [70FEL]). We thus arrive at the discrete equation [94KAR/BLA]

\[
\rho_a(x,t + \tau) = \tilde{\rho}_a(x,t) + \sum_r (\nu_{or,f} - \nu_{or,i}) P_r \prod_{\beta} \tilde{\rho}_\beta^{\nu_{or,i}}(x,t) ,
\]  

(XI.10)
where the sum is over all reactions $r$, the products over all species $\beta$ and

$$
\tilde{\rho}_\alpha(x,t) \equiv p_\alpha \rho_\alpha(x - \lambda, t) + (1 - p_\alpha - q_\alpha)\rho_\alpha(x,t) + q_\alpha \rho_\alpha(x + \lambda, t)
$$

is the result of the transport operation on the particle distribution at time $t$; here $p_\alpha$ and $q_\alpha$ are the species-dependent displacement probabilities.

Up on taking the continuum limit as before, with the additional limiting procedure $P_r \to 0$ so that $P_r/\tau$ remains finite, we obtain the standard transport equations for reacting solutes

$$
\frac{\partial \rho_\alpha(x,t)}{\partial t} = -V_\alpha \frac{\partial \rho_\alpha(x,t)}{\partial x} + D_\alpha \frac{\partial^2 \rho_\alpha(x,t)}{\partial x^2} + \sum_r (\nu_{\alpha,r,f} - \nu_{\alpha,r,i}) k_r \prod_\beta \rho_{\beta}^{\nu_{\beta,i}}(x,t)
$$

where

$$
V_\alpha \equiv (p_\alpha - q_\alpha) \frac{\lambda}{\tau}, \quad D_\alpha \equiv (p_\alpha + q_\alpha) \frac{\lambda^2}{2\tau}, \quad k_r \equiv P_r/\tau.
$$

$k_r$ is the rate constant of reaction $r$.

We emphasize that the CA simulations are not subject to the assumptions which were introduced above with the purpose of deriving the macroscopic equations. The simulations account for microscopic effects of correlations and fluctuations that are typically averaged out by the macroscopic approach. The results of the discrete model were compared carefully to the solution of the reaction-transport PDE’s in Ref. [94KAR/BLA]. Two essential sources of discrepancy were encountered: (i) correlations between the particles that arise as a result of chemical reactions, and (ii) statistical fluctuations. Systematic study shows that the effect of chemically induced correlations disappears as the continuum limit is approached (for details see [94KAR/BLA]). If one sees CA algorithms only as numerical tools for the solution of macroscopic equations, correlations of this type are no more than numerical artefacts associated with the particular method of solution. This is to be contrasted with the potentially observable effect that statistical fluctuations can have on the behaviour of reaction-diffusion systems, as it will be illustrated in Section XI.3.2. Of course, physical systems are after all discrete and so correlations will manifest themselves at some level. Here the discrete model could provide a more accurate model than afforded by the PDE’s.

In reaction-diffusion models with an exclusion principle ones needs to ensure careful book-keeping of the occupied velocity states before and after a reaction. In general there are several species on the lattice and the rotation and propagation operations described previously are applied to each of them independently. The dynamics of different species is coupled by chemical reactions of the type given by Eq. (XI.8). We concentrate, for illustration purposes, on an effective single-species system, assuming the concentrations of other species to be kept constant by contact with an appropriate reservoir [89DAB/BOO,
In the notation of Eq. (XI.8), there is one active species, \( s_1 \), and the reactions \( r \) are identified by the stoichiometric coefficients \( \nu_{r,i} \) and \( \nu_{r,j} \). We denote, for simplicity, \( s_1 \) by \( X \) and \( \nu_{r,i}, \nu_{r,j} \) by \( \alpha, \beta \), respectively. The reaction probability \( P(\alpha\beta) \) is independent of the initial and final velocity states: if, for a given initial configuration, there are \( n_{\alpha\beta} \) possible final velocity configurations of the reaction \( \alpha X \rightarrow \beta X \), each occurs with the same probability \( P(\alpha\beta)/n_{\alpha\beta} \).

Introducing indices \( i_k \) to differentiate between the \( m \) different velocity states \( (i_k = 1, \ldots, m; m = 2 \) for a one-dimensional lattice, \( 4 \) for a two-dimensional square lattice etc.), we note that a reaction configuration is fully defined in terms of \( \alpha, \beta \) and the velocity states \( i_1, \ldots, i_q \) (\( q \equiv |\alpha - \beta| \)) of the particles that are created or destroyed, depending on whether \( \alpha < \beta \) or \( \alpha > \beta \), respectively. With each configuration thus defined we associate a random Boolean variable \( \gamma_{\alpha\beta}(i_1 \ldots i_q) \) which takes the value \( 1 \) when the reaction takes place (with probability \( P(\alpha\beta)/n_{\alpha\beta} \)) and is 0 otherwise. If we then define \( N_i \) as before, we can write the effect of the chemical reaction operation as follows:

\[
N_i \rightarrow N_i + \sum_{\alpha,\beta (\alpha < \beta)} \sum_{i_1,\ldots,i_q \neq i} Q(\{N_i\}, i_1 \ldots i_q) \gamma_{\alpha\beta}(i_2 \ldots i_q) - \sum_{\alpha,\beta (\alpha > \beta)} \sum_{i_1,\ldots,i_q \neq i} Q(\{N_i\}, i_2 \ldots i_q) \gamma_{\alpha\beta}(i_2 \ldots i_q),
\]

where

\[
Q(\{N_i\}, i_1 \ldots i_q) \equiv \prod_{k=1}^\alpha N_{i_k} \prod_{i_1,\ldots,i_q \neq i}^\prime (1 - N_{i_k})
\]

populates the initial state with particles of velocities \( i_1, \ldots, i_q \). The primes constrain the indices of the summation or multiplication to be distinct. In Eq. (XI.14), \( N_i \) increases (decreases) by 1 if a particle with velocity \( i \) is among the \( |\alpha - \beta| \) particles produced (destroyed).

We take the ensemble average of the Eq. (XI.14), defining \( \rho_i \) as the average of \( N_i \) and \( \rho \equiv \sum_i \rho_i \). Assuming that we can factorise the expectation value of products of random variables and taking the continuum limit for a homogeneous system \( (\tau \rightarrow 0, P(\alpha\beta) \rightarrow 0 \), keeping \( P'(\alpha\beta) \equiv P(\alpha\beta)/\tau \) finite), we deduce the rate law

\[
\frac{d\rho(t)}{dt} = \sum_{n=0}^m \kappa_n \rho^n(t), \quad (\text{XI.16})
\]

where

\[
\kappa_n \equiv (-1)^n \binom{m}{n} m^{-n} \sum_{\alpha=0}^n (-1)^\alpha \binom{n}{\alpha} \sum_{\beta \neq \alpha} (\beta - \alpha) P'(\alpha\beta). \quad (\text{XI.17})
\]

Identifying the \( \kappa_n \) with the macroscopic rate constants, one can solve the resulting system of linear equations for the reaction probabilities \( P(\alpha\beta) \). For an inhomogeneous system...
we obtain the standard reaction-diffusion equations. The generalisation to multi-species systems is straightforward [91DAB/BOO, 91KAP/LAW, 92KAP/LAW]. The exclusion principle permits the utilisation of very efficient programming techniques, as described earlier. In the model described in Refs. [89DAB/BOO, 90DAB/LAW, 91LAW/DAB], there are different sets of mesoscopic reaction rules which are consistent with the same macroscopic kinetics. It is possible, however, to construct the reaction probabilities so as to allow only those particle number changes that are specified by the macroscopic mechanism [92WU/KAP, 93GRU/KAP].

XI.3.2. Applications

In this subsection CA modelling will be illustrated by means of applications to various reaction-transport processes. Our goal is to demonstrate the versatility of the method, as well as its ability to describe aspects of the microscopic dynamics, especially when the latter have macroscopic consequences that lie beyond the scope of the standard averaged equations. Thus when microscopic fluctuations determine, under certain conditions, the macroscopic behaviour of physical systems, the mesoscopic level of description afforded by CA models becomes indispensable.

XI.3.2.1. \( a + b \rightarrow c \)

We first consider a homogeneous system consisting of equal amounts of two mobile species, which combine to form an inert species. There is no external supply of reactants, so the two active species will deplete each other until there are only inert particles left. We are interested in the time dependence of the reactant particle density as the final inert state is approached. A system of this kind was analysed in connection with the mutual annihilation of magnetic monopoles and antimonopoles produced in the early universe [83TOU/WIL], but the analysis was relevant to a much wider range of phenomena. Other relevant physical processes include the recombination of electron-hole pairs in semiconductors [80VAR/OCO] and, conceivably, chemical reactions of the type \( a + b \rightleftharpoons c \), if the reverse reaction can be reduced to a negligible rate by varying a physical parameter such as the temperature [78OVC/ZEL].

For a homogeneous system, we write the macroscopic densities of \( a \) and \( b \) as \( \rho_a(t) \) and \( \rho_b(t) \). If the two densities are initially equal, the particular kinetics implies that they will remain so at later times. Then the macroscopic rate equation assumes the simple form

\[
\frac{d\rho_a(t)}{dt} = -k_1\rho_a^2(t),
\]

\( k_1 \) being the rate constant. According to Eq. (XI.18), \( \rho_a \) has the long-time behaviour \( t^{-1} \).

We consider a lattice populated by \( a \) and \( b \)-particles subject to the irreversible reaction \( a + b \rightarrow c \). The species \( c \) plays no active rôle in the evolution of the system. Initially the lattice is occupied by a uniform random distribution of equal numbers of \( a \) and \( b \). We define the densities \( \rho_a(t) \) and \( \rho_b(t) \) by dividing the total numbers of \( a \)- and \( b \)-particles by
the number of sites in the lattice. When $N_a$ $a$-particles and $N_b$ $b$-particles meet at a site, they react with probability $P_1 N_a N_b$, where $P_1 = \tau k_1$. Each time a reaction takes place, one particle of each reactant is subtracted, so that the overall numbers and densities of $a$ and $b$ remain equal to each other. We consider three different cases: (i) the reactants diffuse with the same diffusion coefficient $D$, (ii) the reactants diffuse as before, but one of them is additionally subject to advection with a constant velocity $V$, and (iii) transport is replaced by a random redistribution of the reactants on the lattice. The last case emulates the instantaneous mixing implicitly assumed by the macroscopic rate equation.

The results of our simulations on a one-dimensional lattice are shown in Fig. XI./4. The asymptotic time dependence of $\rho_a$ is $t^{-1/4}$, $t^{-1/2}$ and $t^{-1}$, respectively, in the three cases listed above. In the well-mixed third case, the result coincides naturally with that of the macroscopic equation. When the mixing is less fast, as in the other two cases, a slower depletion mechanism takes over. This happens because, as the bulk of particles disappear in mutual annihilation, the microscopic fluctuations present already in the initial state play an increasingly important rôle. Let us first consider the case of pure diffusion. The time exponent $-1/4$ (which is specific to a one-dimensional system; for $d$ dimensions one finds $-d/4$ for $d < 4$ and $1$ for $d \geq 4$) can be understood as follows [S3T/WIL]: At any given time $t$ in the evolution of an infinite system, particle transport has not had the time to dissolve fluctuations on a length scale longer than $l_D = \sqrt{Dt}$. For $\rho_a(0) = \rho_b(0) = \rho_0$, a part of the system of length $l_D$ contains initially $\sim \rho_0 l_D$ particles of each species and the difference between the numbers of $a$- and $b$-particles is of the order of $\sqrt{\rho_0 l_D}$. Thus the surplus density of the species in excess is of the order of $\sqrt{\rho_0 l_D} / l_D = \rho_0^{1/2} (Dt)^{-1/4}$. We see that the decay of initial fluctuations results in a $t^{-1/4}$ decline of the density which is bound to dominate over the $t^{-1}$ decline due to bulk depletion for long times. For very long times the system breaks up in segregated regions of $a$- or $b$-particles formed by the remaining excess particles after the bulk has annihilated; the reaction then proceeds only along the boundaries of these regions. It turns out that the relative drift between the reactants mixes them faster than diffusion and the asymptotic decline of the density follows a $t^{-1/2}$ law. This can be easily seen if the length scale $\sqrt{Dt}$ swept out by diffusion is replaced by the advective scale $Vt$ [85KAN/RED]. It is clear that, with the exception of the unphysical case of infinitely fast transport, the correct long-time decline of the density can only be captured if microscopic fluctuations are explicitly accounted for. To the extent that a mesoscopic model is called for, it is obviously desirable that it should be able, like the model used here, to account for advection, which was seen to alter qualitatively the behaviour of the physical system under consideration.

XI.3.2.2. Autocatalytic reactions

As we saw in Section XI.3.1, CA can be used to model species of different transport properties, as well as complex chemical reactions. We are now going to consider reaction-diffusion systems in which the difference between the diffusion coefficients of the reactants and a certain degree of complexity in the reactions play an essential rôle in the observed phenomena. The reactions of interest here contain autocatalytic steps, in which the
Figure XI.4: $\alpha$-density for a one-dimensional, homogeneous system reacting via $a + b \rightarrow c$, as a function of time: (a) only diffusion (solid line), (b) diffusion+relative advection (dashed line), and (c) random redistribution (dotted line).

catalyst is one of the products (e.g., $2X + Y \rightarrow 3X$). When autocatalytic systems are maintained far from chemical equilibrium (e.g., by suppressing reverse reactions and by removing or adding reactants), they can experience phase transitions to states with remarkable spatial or temporal structures. A classic example is the Belousov-Zhabotinsky reaction (i.e., the oxidation of citric, malonic or bromomalonic acid by bromate in acidic aqueous solution, with variable valence ions, such as $\text{Ce}^{4+}/\text{Ce}^{3+}$ or $\text{Fe}^{3+}/\text{Fe}^{2+}$, acting as catalysts [58BEL2, 64ZHA, 70ZAI/ZHA]), which, under appropriate conditions, displays oscillations in the concentrations of the oxidised and reduced forms of the catalyst, as well as periodic propagation of concentration waves. The emergence of ordered states far from equilibrium is of extreme importance in chemistry and biology [77NIC/PRI, 89MUR].

There is a certain class of steady spatial structures which are sustained by the combined effect of reaction kinetics and diffusion. The earliest example was proposed by Alan Turing in 1952 [52TUR]. A crucial condition for the formation of such patterns is that two species have different diffusion coefficients. Then it is possible that a uniform steady state, which would be stable in the absence of diffusion, becomes unstable and goes over to a stationary spatial concentration pattern when the ratio of diffusion coefficients exceeds a certain critical value. The faster species, the *inhibitor*, hinders by chemical action the production of the slower one, the *activator*, and confines the latter to restricted regions of
space, giving rise to a pattern of inhomogeneous concentration. The inhibitor itself forms a complementary pattern of high and low concentration. One can apply linear stability analysis to the reaction-diffusion equations to derive the range of wavelengths that become unstable for given values of the macroscopic parameters. The emerging pattern is an example of spatial symmetry breaking since it defines a new length scale that does not depend on the geometrical properties of the system, but rather on intrinsic properties described by the diffusion coefficients and the reaction rates (including feed and removal rates of reactants, as well as prescribed concentrations of external reactants). Sustained concentration patterns were obtained recently with the chlorite-iodide-malonic acid reaction in open reactors, in which the reactants diffuse into an inert gel from adjacent reservoirs of constant and uniform concentrations [90CAS/DUL, 91KEP/CAS, 91QUY/SWI].

One of the simplest reaction systems that are subject to the Turing instability under appropriate conditions is

\[
X \xrightleftharpoons[k_1]{k_2} A, \quad 2X + Y \rightarrow 3X, \quad B \rightarrow Y, \tag{XI.19}
\]

which was conceived by J. Schnackenberg in his search for simple systems admitting periodic solutions [79SCH2]. The concentrations of \(A\) and \(B\) are held fixed, for example by external supply or removal of reactants. The system (XI.19) can be analysed analytically and is known to exhibit a Turing instability for a wide range of parameter values [89MUR]. If the first reaction in (XI.19) is made irreversible, the system may still oscillate, but it may also evolve towards infinite concentrations (e.g., \(X \rightarrow 0, Y \rightarrow \infty\), with \(X^2Y\) finite); the system \(X \rightarrow A, 2X + Y \rightarrow 3X, B \rightarrow Y\) had been used earlier by E. E. Selkov to model the phosphofructokinase catalysed production of ADP from an ATP substrate, as a possible source of glycolytic oscillations [68SEL, Eq. (II)]. Replacing the last reaction in Selkov’s scheme with the pair of reactions \(B + X \rightarrow Y + D, E \rightarrow X\), we obtain the “Brusselator”, one of the earliest systems employed to illustrate the possibility of symmetry breaking instabilities [68PRI/LEF].

Simulations of the above reaction systems have been performed with CA models [91KAP/LAW, 92KAP/LAW, 93DRO/FRA, 93KAR, 94KAR/BLA]. The pattern in Fig. XI.5 was obtained from a random, macroscopically homogeneous initial state after a few thousand iterations of a CA simulation of the Schnachenberg model on a two-dimensional lattice with periodic boundary conditions [93KAR, 94KAR/BLA]. Given the rest of the macroscopic parameters, linear stability analysis predicts in this case that the Turing instability occurs if the ratio of diffusion coefficients \(d \equiv D_Y/D_X\) exceeds the critical value \(d_{crit} = 19.7\). The simulation was performed with \(d = 30\), for which the macroscopic analysis predicts a window of unstable wavelengths consistent with the observed pattern.

Whereas reaction-diffusion equations describe the evolution of the macroscopically averaged particle densities, CA simulations incorporate microscopic fluctuations at all stages of the evolution. Fluctuations are expected to have an enhanced influence on the dynamics of the system near bifurcation points, such as near the onset of the Turing instability in
Figure XI.5: Spatial concentration pattern obtained from two-dimensional simulation of
the Schnackenberg model.

parameter space. The computational efficiency of CA models with an exclusion principle
allows their application to detailed investigations of the rôle of fluctuations in particular
chemical systems. Thus, in two-dimensional simulations of the Schnackenberg model, as
well as of the Selkov model, transient patterns appear also below the critical value of the
diffusion coefficient ratio [91KAP/LAW, 92KAP/LAW, 93DRO/FRA]. In that region pat-
tern formation is not possible according to the macroscopic reaction-diffusion equations.
Apparently, below the critical ratio, the homogeneous state is destabilised by density
fluctuations which effectively widen the range of unstable wavenumbers. For parameter
values for which the macroscopic equations predict a Turing instability, the patterns ob-
tained by CA simulation generally display a certain roughness and are less regular than
the ones derived from the reaction-diffusion equations. Whereas the latter patterns are
strictly stationary after a certain time, the former are continually perturbed by fluctua-
tions which occasionally destabilise a sustained structure and induce reorganisation of
the pattern (Fig. XI.6).

XI.3.2.3. Reactions with mineral surfaces

We now move to chemical reactions taking place in heterogeneous systems, where different
phases are in contact with each other. Thus, solutes often react with the surfaces of the
water-conducting channels along which they are transported. The reaction may be in the
form of mineral precipitation and dissolution, which leads to changes in rock properties
(e.g., the porosity) with a direct impact on the transport of the reacting solutes. Alter-
natively, the solid surface may act as a catalyst by adsorbing one or more reactants from
the liquid or gaseous phase and modifying them so that they react more readily. In both
Figure XI.6: Turing pattern reorganisation (from four to three stripes) caused by density fluctuations. The density pattern shown here (see grey scale) is unpublished work by D. Dab and was obtained with the Maginu model [75MAG, 79MAG] simulated on a 256 × 256 lattice with parameter values $k = 0.9$, $c = 0.45$, $s = 10$, $D_x = 1$ and $D_y = 19$, as described in Refs. [91DAB/BOO, 92DAB].
cases, inhomogeneities in the spatial distribution of reactants play a crucial rôle in the evolution of the system, while moving boundaries may further complicate the situation. Due to its ability to treat spatially and temporally varying parameters with no additional effort, the CA approach is particularly appropriate for modelling systems of the kind described here. We shall illustrate this by means of two simple CA models of heterogeneous processes.

We first consider the precipitation/dissolution reaction

\[ c(s) \xrightleftharpoons{K_1 \rightarrow K_2} a + b, \]  

where \( a \) and \( b \) are aqueous species, \( c \) is a mineral and \( K_1, K_2 \) are the rate constants. For constant and uniform porosity \( \varepsilon \), the standard reaction-transport equations for this system are

\[
\begin{align*}
\varepsilon \frac{\partial C_a(x,t)}{\partial t} &= -\varepsilon V_a \frac{\partial C_a(x,t)}{\partial x} + \varepsilon D_a \frac{\partial^2 C_a(x,t)}{\partial x^2} + \zeta \left( K_1 - \varepsilon^2 K_2 C_a(x,t)C_b(x,t) \right), \\
\frac{\partial C_c(x,t)}{\partial t} &= -\zeta \left( K_1 - \varepsilon^2 K_2 C_a(x,t)C_b(x,t) \right),
\end{align*}
\]

where \( C_a \) and \( C_b \) are the concentrations of the solutes in mol per m\(^3\) of water, \( C_c \) is the “concentration” of solid in mol per m\(^3\) of rock and \( \zeta \) is a constant with

\[ \zeta = \begin{cases} 1, & \text{if } C_c(x,t) > 0 \text{ or } C_a(x,t)C_b(x,t) > K, \\ 0, & \text{otherwise} \end{cases} \]

\( K \equiv K_1/\varepsilon^2 K_2 \) being the solubility product. The equation for \( C_b \) is analogous to the one for \( C_a \).

In the simulation, the \( a \)- and \( b \)-particles are mobile, whereas the \( c \)-particles are stationary. The reaction rule depends on the local numbers of \( a \) and \( b \) as in the case of the reaction \( a + b \rightarrow c \) considered above, but it additionally depends on the numbers of reactants through the conditions for the onset of precipitation. Precipitation may namely occur only if there is solid already present or if the solution is saturated (the definition of \( \zeta \) above is the mathematical equivalent of this statement). This leads to the following mesoscopic rule: If one or more \( c \)-particles are present at a site, one of them goes into solution in the form of an \( a \)- and a \( b \)-particle with probability \( P_1 \). If \( N_a \) \( a \)-particles and \( N_b \) \( b \)-particles are present, then they may precipitate and form a \( c \)-particle only if at least one \( c \)-particle is already present or if the product of the densities of \( a \) and \( b \) (calculated by averaging over an ensemble of macroscopically identical systems) is greater than \( P_1 / P_2 \). If one or both of these conditions are fulfilled, precipitation is allowed to take place with probability \( P_2 N_a N_b \). Particle densities are related to the physical quantities in Eq. (XI.21) by \( C_a = \gamma \rho_a \), \( C_b = \gamma \rho_b \) and \( C_c = \gamma \varepsilon \rho_c \), where the scaling factor \( \gamma \) can be fixed by the
are chosen to be consistent with calcite/carbonates for dissolution and precipitation are
unable mineral with a density of 2.71 g/cm³. The left half of the rock is occupied at time \( t = 0 \) by a soluble mineral with a density of 2.71 g/cm³ and a molecular weight of 100. The rate constants for dissolution and precipitation are \( K_1 = 1.3 \times 10^{-3} \text{ mol} \cdot \text{m}^{-3} \cdot \text{s}^{-1} \) and \( K_2 = 0.93 \text{ m}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1} \), respectively; they are compatible with a solubility product of \( K = 10^{-2.48} \text{ mol}^2 \cdot \text{m}^{-6} = 10^{-8.48} \text{ (mol/l)}^2 \). The physical and chemical parameters are chosen to be consistent with calcite (CaCO₃) as a typical mineral in the geological systems of interest. The value of \( K_1 \) in particular follows from the value of the dissolution rate per unit surface of mineral, \( K_{1s} = 6.5 \times 10^{-11} \text{ mol} \cdot \text{cm}^{-2} \cdot \text{s}^{-1} = 6.5 \times 10^{-7} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \) obtained in an investigation of the pH dependence of the dissolution rate of various carbonates at 25°C using a fluidized bed reactor [89CHO/GAR]. To obtain the dissolution rate per unit volume of mineral, we have multiplied \( K_{1s} \) by a surface area to volume ratio of 20 cm⁻¹, which corresponds to grains of size 0.3-0.4 cm. It is clear that \( K_1 \) is inversely proportional to the grain size and a good knowledge of the latter is necessary for modelling dissolution kinetics in particular situations. The value of \( K_2 \) is then calculated from \( K_2 = K_1/\varepsilon^3 K \) and is consistent within 2-3% with the value of \( K_{1s} \) found independently in Ref. [89CHO/GAR]. The dissolved species Ca²⁺ and CO₃²⁻ move with an advection velocity of \( V = 10^{-5} \text{ m/s} = 0.86 \text{ m/day} \) and a diffusion coefficient of \( D = 10^{-9} \text{ m}^2/\text{s} \). For the simulation we choose \( \lambda = 10^{-5} \text{ m}, \tau = 0.05 \text{ s} \) and \( \gamma = 1.0 \text{ mol/m}^3 \).

Fig. XI.7 shows the profiles of \( C_s \) and \( C_a \) at time \( t = 10^4 \text{ s} = 2.8 \text{ h} \).

In the simulation we obtain net precipitation of solid downstream from the original solid edge. Due to fluctuations in the solute densities, the product of these densities occasionally exceeds the saturation threshold and precipitation ensues. This effect is absent from the macroscopic description, where the edge remains sharp. The net precipitation of solid in the right half of the lattice is accompanied by a reduction in solute concentration relative to the prediction of the macroscopic equations. Of course the amount of solid that is found downstream of the edge is tiny on the scale of the total amount of solid, but the consequences can be more serious for the concentration of solutes. In Fig. XI.7, of 7.3 million solid particles initially present, about 750 have been removed from the solid block and about 110 have precipitated in the right half of the lattice. This suffices however to produce a 20% suppression in the solute concentration, as a comparison of the dotted and dashed curves shows. Simulations show that the downstream precipitation of solid and the suppression of solute concentration diminish as we reduce the magnitude of the statistical fluctuations by increasing the size of the ensemble over which we average. Since the particles of our simulations do not model individual molecules of the actual system, the interpretation of statistical fluctuations and their consequences is not immediately obvious. We can assume a phenomenological point of view, allowing for microscopic processes not explicitly accounted for to contribute to the fluctuations present in our
Figure XI.7: Profile of solute concentration (horizontal dotted line and solid line running on the average parallel to it: reaction transport equations and CA, respectively; the short-dashed line is a smoothed version of the solid line; axis labelled on the right) and the “concentration” of solid per m$^3$ of rock (vertical long-dashed line and solid line running partly parallel to it: reaction transport equations and CA, respectively; axis labelled on the left).

model. Then one has to normalise the amplitudes of the fluctuations by comparing the size of the resulting effects with real systems. The impact of the observed effect will therefore depend on the problem at hand. For times long enough for precipitation/dissolution to cause changes in the porosity, it is likely to influence those changes, to a degree however that remains to be investigated.

Remarkably, the effect described above occurs only in the presence of advection and is absent when diffusion is the only transport mechanism. The dependence of the effect on the physical parameters of the problem was studied in Ref. [95KAR2]. It was found there that the suppression of solute concentration downstream from the solid edge persists up to the longest times $t$ for which the simulation can be performed without exceeding a week of CPU time. If one varies the relative time scales for transport (especially advection) and reactions, then the effect of fluctuations is washed out when the reaction kinetics is not fast enough to keep up with transport. The effect appears clearly only when transport is slow relative to the kinetics. These observations underline the important role of advection in the interplay between transport and chemistry. The ability of the mesoscopic model used here to account for advection clearly opens a wide field of interesting phenomena to be investigated.
As another example of a heterogeneous process we take up the catalytic oxidation of CO(g) on platinum (Pt) surfaces. This process was investigated in Ref. [92WU/KAP] from the point of view of the interplay between sorption kinetics, reactions and surface phase transformations. The basic process consists of the following steps: gaseous CO and O₂ adsorb on sites of the Pt(111) surface and O₂ molecules dissociate to O atoms, which oxidise adsorbed CO to form CO₂. The adsorption rates of CO(g) and O₂(g) depend on the availability of free surface sites. Adsorbed CO and O may of course desorb before they react, but, once they react, CO₂ desorbs rapidly. If ρ₁ and ρ₂ are the densities of adsorbed CO and O respectively (note that 1 and 2 are here species labels), the summation over velocity states having already been performed) and ρ₀ the (constant) density of adsorption sites (free + occupied), one can write down schematically the rate equations

\[
\begin{align*}
\frac{d\rho_1}{dt} &= k_1 p_{CO} (\rho_0 - \rho_1 - \rho_2) - k_{-1} \rho_1 - k_0 \rho_1 \rho_2 \\
\frac{d\rho_2}{dt} &= k_2 p_{O_2} (\rho_0 - \rho_1 - \rho_2)^2 - k_{-2} \rho_2^2 - k_0 \rho_1 \rho_2 ,
\end{align*}
\]

where \( k_1 \) \((k_{-1})\) and \( k_2 \) \((k_{-2})\) are the adsorption (desorption) rate constants of CO and O₂, \( p_{CO} \) and \( p_{O_2} \) are the respective partial pressures and \( k_0 \) is the rate constant for the surface reaction \( CO + O \rightarrow CO_2 \). The first term on the right hand side of both rate equations makes explicit the dependence of adsorption rates on the density of free sites.

If the CO-O reaction takes place on the Pt(100) crystallographic plane, then the surface may undergo phase transformations, depending on the fraction of sites covered by CO. Thus, if the surface is in the hexagonally ordered phase (hex) and the CO coverage exceeds \( \sim 90\% \) a transition occurs to the \((1 \times 1)\) phase characterised by a square lattice of surface atoms on which CO molecules occupy alternate sites. When the CO coverage falls below \( \sim 30\% \) the reverse surface transformation takes place. Since a reorganisation of the surface affects the sorption rates and, hence, the oxidation kinetics, the coupling between the different processes can induce oscillations in the surface concentration of the reactants and the fraction of sites in each phase. These oscillations proceed by means of the appearance and growth of domains of one phase in the midst of the other, coupled with the diffusion of adsorbed particles across the domains. Such oscillatory behaviour has been observed experimentally [84NOR/BIN].

The model of Ref. [92WU/KAP] applies an exclusion principle, as described in Section XI.3.1, making sure, however, that the reactive transitions at the mesoscopic level are only those implied by the rate law Eq. (XI.23). Extending the notation used earlier for one-species systems, we introduce the probability \( P(\alpha|\beta) \) for the transition \( \alpha_1 CO + \alpha_2 O \rightarrow \beta_1 CO + \beta_2 O \), with \( \alpha \equiv (\alpha_1, \alpha_2) \) and \( \beta \equiv (\beta_1, \beta_2) \). \( P(\alpha|\beta) \) is written as

\[
P(\alpha|\beta) = p_1(\alpha) \delta_{\beta_1,\alpha_1+1} \delta_{\beta_2,\alpha_2} + p_2(\alpha) \delta_{\beta_1,\alpha_1-1} \delta_{\beta_2,\alpha_2} + p_3(\alpha) \delta_{\beta_1,\alpha_1} \delta_{\beta_2,\alpha_2+2} \\
+ p_4(\alpha) \delta_{\beta_1,\alpha_1} \delta_{\beta_2,\alpha_2-2} + p_5(\alpha) \delta_{\beta_1,\alpha_1} \delta_{\beta_2,\alpha_2-1} .
\]

In Eq. (XI.24), the \( p_i(\alpha), i = 1, \ldots, 5 \), are the probabilities for CO adsorption and
desorption, O adsorption and desorption, and CO oxidation, respectively:

\[
\begin{align*}
p_1(\alpha) &= \begin{cases} 
\tilde{k}_1 (m - \alpha_1 - \alpha_2), & \text{if } \alpha_1 + \alpha_2 < m, \\
0, & \text{if } \alpha_1 + \alpha_2 \geq m,
\end{cases} \\
p_2(\alpha) &= \tilde{k}_{-1} \alpha_1, \\
p_3(\alpha) &= \begin{cases} 
\frac{1}{2} \frac{k_2 (m - \alpha_1 - \alpha_2) (m - 1 - \alpha_1 - \alpha_2)}{k_1}, & \text{if } \alpha_1 + \alpha_2 < m - 1, \\
0, & \text{if } \alpha_1 + \alpha_2 \geq m - 1,
\end{cases} \\
p_4(\alpha) &= \frac{1}{2} \tilde{k}_{-2} \alpha_2 (\alpha_2 - 1), \\
p_5(\alpha) &= \tilde{k}_0 \alpha_1 \alpha_2.
\end{align*}
\]

If one chooses the parameters \(\tilde{k}_i\) according to

\[
\begin{align*}
\tilde{k}_0 &= k_0, \\
\tilde{k}_1 &= k_1 p_{\text{CO}}, \\
\tilde{k}_{-1} &= k_{-1} \\
\tilde{k}_2 &= \frac{m}{m - 1} k_2 p_{\text{O}_2}, \\
\tilde{k}_{-2} &= \frac{m}{m - 1} k_{-2},
\end{align*}
\]

one obtains upon averaging and taking the continuum limit rate equations very similar, but not identical, to Eq. (XI.23). There is a clear connection between the different terms in the rate equations (XI.23) and the corresponding expressions for the \(p_i(\alpha)\), which are reminiscent of Eq. (XI.9).\(^5\) Eqs. (XI.24), (XI.25) and (XI.26) define the mesoscopic reaction dynamics.

The phase transformations of the surface can also be modelled by a CA rule. Thus one ascribes each site to one of two phases and allows it to make a transition to the other phase with a certain probability, if the local CO coverage crosses a certain critical value. The CO coverage at a site is defined by counting the number of CO molecules in a neighbourhood consisting of the site itself and its nearest neighbours. The phase transition couples back to the adsorption and reaction kinetics, since the reaction rates \(k_i\) have different values for each phase.

Fig. XI.8 shows the oscillations in the CO surface density obtained for a particular choice of the physicochemical parameters [92WU/KAP]. Initially most of the sites are in the hex phase which adsorbs O much more weakly than the \((1 \times 1)\) phase. As a result the CO density increases (Fig. XI.8a), the critical coverage for transition to the \((1 \times 1)\) phase is locally exceeded and domains of that phase begin to appear and spread (Fig. XI.8b). These domains adsorb O at a high rate and cause oxidative depletion of the CO molecules that are originally present in their interior, as well as of those that arrive there by diffusion. Thus the new phase wins gradually over and the density of adsorbed CO diminishes (Fig. XI.8c). When, however, the CO coverage falls locally below a certain critical value, domains of the original phase begin to appear and spread (Figs. XI.8d,e) and the CO density increases again (Fig. XI.8f). Thus the relatively

---

\(^5\) The \(\alpha_i\) in Eq. (XI.25) cannot exceed, however, the number of possible velocity states and obey a binomial distribution at equilibrium, whereas the \(N_a\) in Eq. (XI.9) are unrestricted and have a Poisson equilibrium distribution.
Cellular automata for transport with chemical reactions

Figure XI.8: Oscillations in CO surface density obtained from two-dimensional simulation of CO catalytic oxidation on the Pt(100) plane. (reprinted with permission from Ref. [92WU/KAP], Fig. 5). The frames (a)-(l) are for times $t = 100$-$1200$ at equally spaced time intervals of 100 time steps. The simulation was carried out on a $100 \times 100$ hexagonal lattice with periodic boundary conditions. For the values of system parameters used in the simulation the reader is referred to [92WU/KAP].

\[ \text{Figure XI.8: Oscillations in CO surface density obtained from two-dimensional simulation of CO catalytic oxidation on the Pt(100) plane. (reprinted with permission from Ref. [92WU/KAP], Fig. 5)} \]
simple CA we are considering here is capable of reproducing the experimentally observed oscillatory behaviour. Moreover, as the Pt surface oscillates in space and time between the two phases, which are characterized by different reaction rate constants, the present application illustrates the capacity of CA models to describe systems with spatially and temporally varying parameters.

It should be remarked that both models of heterogeneous processes that we have presented are relatively simple. They already show the potential of the mesoscopic method to describe interesting physical behaviour, but they should rather be taken as the basis for more elaborate and realistic models.

XI.4. Conclusion

The models of reaction-transport phenomena discussed in this chapter occupy a position intermediate between the standard macroscopic approach of partial differential equations (PDE's) and the fully microscopic approach of molecular dynamics. We have indicated with several examples that there is a wide range of physical phenomena for which the mesoscopic point of view provides the necessary amount of detail (that PDE's cannot afford) and optimises the use of resources (by neglecting inessential details of the microscopic dynamics). Cellular automata (CA) describe transport and chemical reactions at an elementary level, keeping, however, only those aspects of the microscopic dynamics which are important for the problem at hand. Due to their simplicity, CA models are conceptually transparent and can be transcribed into simple computer code. This is a significant advantage when it comes to modelling complex geometries and boundary conditions or the kinetics of arbitrary chemical reactions. CA algorithms iterate integer variables and are therefore free of round-off errors and associated instabilities. This remains true for the stochastic CA models considered here, since real numbers appear only as bounded probabilities. By being faithful to the local and parallel character of the physical processes they model, cellular automata are suitable for implementation on massively parallel computers. It should be emphasised that it was largely the dramatic progress in computer hardware and architecture in recent years that made CA modelling of natural phenomena technically possible.

The models we have discussed simulate the transport of particles as a random walk on a regular spatial lattice. When the particles meet at a lattice site, they react chemically and are transformed according to a local probabilistic rule. Radioactive decay, sorption on conduit walls and the dissolution of solids are also modelled by simple probabilistic rules. We have presented a model which places no restriction on the number of particles that can be found at a site, as well as one derived from lattice gas automata for fluid dynamics, which allows only a small set of possible velocity states to each particle. The “particles” in both models are mathematical abstractions of the actual molecules of the physical system. The number of particles is large enough to make statistical concepts meaningful, but is still many orders of magnitude smaller than the real number of molecules involved. Mesoscopic modelling relies crucially on the assumption that this is legitimate, provided that the macroscopic behaviour of interest does not depend on the details of the microscopic
dynamics, but follows from general properties of the latter. Of the two models, the former has the merit of being able to account for advection by imparting a directional bias to the random walk and of modelling chemical reactions in a more transparent and flexible way. The lattice gas model, on the other hand, offers substantial computational advantages: thanks to the limited number of allowed particle configurations at a site, it can be programmed at bit level (thus making optimal use of computer memory and processing power) and updating can be optimised by using look-up tables (which contain stored all elementary events that can take place at any site). The ability to describe advection and a relative ease in the inclusion of various chemical reactions are indispensable for modelling coupled transport and reaction phenomena in geological media, but computational performance is an important criterion of the usefulness of a model as a practical tool. Despite the recent advances in computer resources, computational efficiency still has to be reckoned with, especially for problems of the complexity we wish to address. It is therefore desirable to combine the advantages of the simple and more flexible model with the experience accumulated with numerous specific applications of lattice gas models.

In the simulations discussed here, the transport of solutes was modelled assuming that their advection followed a given velocity field. If the solute concentration is small enough, the velocity field coincides with that of pure water flowing under the given mechanical conditions. The dynamics of water flow is governed by the Navier-Stokes equations, which for a porous medium go over to Darcy’s law. Although the applications presented here involved only uniform flows, the transport model without an exclusion principle was formulated for an arbitrary flow field. In general the problem of solute transport can be solved by a two-step procedure, where one first solves the appropriate hydrodynamic equations and then uses the resulting velocity field as an input parameter to the model describing solute transport. This approach is conceptually similar to the Lagrangian approach for modelling tracer transport in geological formations (e.g., Ref. [82PRI/NAY]). Chemical reactions can be added and the full algorithm iterated in time. If the porosity and the permeability of a porous medium change substantially as a result of chemical reactions, the influence of these changes on water flow have to be explicitly considered.

To quantify computational efficiency in CA simulations, one usually introduces the concept of site updates per second (u.p.s.). The density of particles has an influence on updating speed, but, except for simulations with very different particle densities, it is useful to compare the performance of various algorithms in terms of u.p.s. We consider first the model with no a priori limitation on the number of particles per site. The simulation of the reaction \( a + b \rightarrow c \) that produced the solid curve in Fig. XI.4, had an average performance of \( 1.2 \times 10^6 \) u.p.s. and required about 16 CPU hours on a massively parallel Connection Machine (CM-200). The pattern shown in Fig. XI.5 took about 30 CPU hours at a rate of \( 2 \times 10^4 \) u.p.s. on a VAX-9000 in scalar mode (the simulation of the reaction \( a + b \rightarrow c \) on the same computer was roughly a factor of 4 less efficient than on CM-200). The simulations can be made faster by utilising a low-level instruction set available on the Connection Machine, but this would impair the transparency of the code. The potential of application-specific optimisation becomes clear if we compare the above rates with those achieved with specialised lattice gas models. Thus, the reaction \( a + b \rightarrow c \)
was simulated with a lattice gas model using a look-up table on a CRAY-YMP at a rate of $2 \times 10^5$ u.p.s., while a four times higher rate was attained on a CM-2a (typically slower than CM-200 by a factor of 2) [91CHO/DRO2]. It should be mentioned, however, that the code without limitation on particle number was applied unmodified to the case with advection (the dashed curve in Fig. XI.4) at no cost in performance, whereas advection lies beyond the scope of the lattice gas model.

The relative merits of different CA models and standard numerical methods for the solution of the corresponding PDE's depends on the specific applications. Thus, with present-day computers, pattern formation in autocatalytic reaction systems can be studied in general more efficiently with conventional methods; if, however, one is interested in the role of fluctuations, the mesoscopic approach provides a powerful alternative. It is, therefore, important to seek areas of applications where each method maximises its advantages. CA models are very well suited for describing transport with inhomogeneous and time-varying parameters. They also naturally describe the chemical kinetics of systems which are not in chemical equilibrium. According to the discussion in the Introduction, the guaranteed stability of CA algorithms is a valuable asset when non-linear processes come into play. Finally, the ability of cellular automata to accommodate arbitrary boundary conditions (including moving boundaries) has not been sufficiently exploited so far. Among potential applications suitable for CA modelling, of particular theoretical and practical interest are the interaction of solutes with the solid surfaces of porous and fractured media and the coupling of porosity changes, induced by precipitation/dissolution, with solute transport. CA models appear to be particularly called for when, for example, the physical processes of interest show strong variations in space [92SAR/BRA] or when chemical reactions are slow compared to transport [90WOL]. It is in such cases, where conventional methods are confronted with serious conceptual and technical problems, that cellular automata can best utilise their potential for incorporating microscopic detail in the macroscopic description of the physical world.

XI.5. Acknowledgements

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